

## EFFECT OF IRON CATALYSTS ON HYDROGENATION PATHWAYS IN DIRECT COAL LIQUEFACTION

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### Abstract

The effect of a commercially available, high surface area nanometer size iron oxide (SFIO) catalyst on the pathway by which hydrogen is added to a subbituminous coal during direct liquefaction was studied under a variety of conditions. This unique iron oxide, prepared by pyrolyzing volatilized iron carbonyl to produce a finely divided product, is characterized as  $\gamma\text{-Fe}_2\text{O}_3$  having a surface area of  $\sim 300\text{ m}^2/\text{g}$  and particle size of 1-3 nm. Liquefying Wyodak coal in tetralin (0.5 hrs, 415 °C, 2.3 tetralin/dry coal, 6.89 MPa  $\text{H}_2$  cold) containing 1.2 wt % Fe as SFIO resulted in an increase in overall coal conversion (77 to 83%) with most of the increase in product being in formation of THF soluble-pentane insoluble product. Adding an excess of sulfur to convert the iron to pyrrhotite further increases conversion to 85% along with a decrease in the THF soluble-pentane insoluble fraction. The presence of catalyst increases the amount of hydrogen added to the product as dihydrogen ( $\text{H}_2$ ) relative to the amount from tetralin via the H-donor pathway. In the absence of catalyst, 60% was added as  $\text{H}_2$ ; adding 1.2% Fe increased  $\text{H}_2$  addition to 67%; adding 3 mol S/mol Fe to 1.2% Fe further increased  $\text{H}_2$  addition to 82%.

### Introduction

Through the use of various types of catalysts, high yields of distillate fuels have been produced in pilot plants from lower-cost subbituminous coal.<sup>1,2,3</sup> The use of high surface area, small particle catalysts has been one area that has been extensively explored in an effort to maximize yields and reduce the cost of catalyst. Fe has been of particular interest as a dispersed catalyst because of its abundance, low cost and its environmental acceptability. Various approaches have been used for preparing disposable nanometer size Fe catalysts, among which are microemulsions,<sup>4,5</sup> aerosols,<sup>6,7,8,9</sup> hydrothermal disproportionation of sulfides,<sup>10</sup> and precipitation of sulfated oxyhydroxides.<sup>11</sup> Highly dispersed iron particles, in various forms as oxides and oxyhydroxides, have been shown to retain their small size upon conversion to pyrrhotite under coal hydroliquefaction conditions.<sup>4,7,12</sup>

In our laboratory, a specially prepared, commercially available superfine Fe oxide (SFIO) was found to have high activity for coal conversion and excellent selectivity for producing distillate product.<sup>13</sup> In the study reported here, the activity of this catalyst for conversion of a Wyodak coal in tetralin was compared with a much lower surface area Fe oxide prepared from Aiusruther spray roast processing of spent acid from steel pickling.<sup>14</sup> The effect of these catalysts on the pathways by which hydrogen (H) is added to the coal and its products was investigated.

### Experimental

Samples of the subbituminous coal and powdered iron oxides used at the Wilsonville Advanced Coal Liquefaction Facility in Run 263J<sup>14</sup> were supplied by CONSOL, Inc. The Wyodak coal from the Black Thunder mine in Wright, Wyoming was ground to -200 mesh, riffled and stored under nitrogen at 4 °C. Proximate and ultimate analyses are presented in Table I. The average moisture content measured at the beginning of each run was  $21.9 \pm 0.72$  wt % of as-received coal.

Two iron oxide catalysts were used. One, a sample of SFIO provided by MACH I, Inc., King of Prussia, PA, contained 63 wt % Fe with a  $\gamma\text{-Fe}_2\text{O}_3$  structure, average particle size of 1-3 nm, and nitrogen BET surface area of  $300\text{ m}^2/\text{g}$ .<sup>15</sup> The second, from Bailey Engineers, Fairfield, AL, (IO) was 99%  $\text{Fe}_2\text{O}_3$  with 0.35 wt % manganese oxide being the largest impurity. The material had a structure of  $\alpha\text{-Fe}_2\text{O}_3$ , nitrogen BET surface area of  $8.6\text{ m}^2/\text{g}$ , an average particle size of  $\sim 140$  nm, and bulk density 26 times greater than SFIO (1.37 vs. 0.052 g/ml). Carbon black (CB) was purchased from UIC, Inc. and had a fixed carbon content of 93% with a nitrogen BET surface area of  $90\text{ m}^2/\text{g}$ .

Liquefaction experiments were conducted by adding 3 grams of coal, 5.4 grams of tetralin, and catalyst to a 50 mL microautoclave. When used, dimethyl disulfide (DMDS) was added at a ratio of 3.0 moles S per mole Fe. The reactor was sealed, pressurized with  $\text{H}_2$  to 6.89 MPa, and immersed in a fluidized sand bath set at the specified temperature while continuously agitating at a rate of 400 cycles per minute. After the specified reaction period, the microautoclave was rapidly cooled in a sand bath at room temperature. Gaseous products

were collected and analyzed by gas chromatography. Solid-liquid products were washed from the reactor using tetrahydrofuran (THF) and extracted in a Soxhlet apparatus for 18 hours. The THF-insoluble material (IOM), comprising unconverted macerals and mineral matter, was dried (80 °C/0.1 atm). A pentane insoluble-THF soluble fraction (PA+A) was precipitated from the concentrated THF soluble fraction by adding pentane. The pentane soluble material (Oils) was analyzed with a Hewlett-Packard 5890 gas chromatograph fitted with a DB-5 column to determine the naphthalene-tetralin ratio. Product yields were calculated assuming complete recovery of the inorganic mineral matter plus catalyst, which was demonstrated independently. Fe in the catalyst precursor is presumed to convert to pyrrhotite ( $\text{Fe}_{9.5}\text{S}$ ) and report to the ash fraction. Oils are calculated by difference, which includes water produced during the reaction and any experimental error. The net product yield equals the amount of maf coal in the feed and coal conversion equals 100 minus the yield of IOM. The average standard deviations for each product fraction were calculated: hydrocarbon gases, 0.1;  $\text{CO}+\text{CO}_2$ , 0.4; IOM, 1.4; PA+A, 2.4; Oils, 2.8.

## Discussion

The dominant phase of the SFIO, as determined by X-ray absorption fine structure (XAFS) analysis, is  $\text{FeOOH}\cdot x\text{H}_2\text{O}$  with bulk iron coordinated to six oxygen or hydroxyl groups along with a significant additional fraction of the iron located at the particle surfaces at sites with lower coordination.<sup>16</sup> Extended heating at temperatures  $>400^\circ\text{C}$  produces  $\alpha\text{-Fe}_2\text{O}_3$ . Considerable particle growth occurs upon sulfidation in the presence of  $\text{H}_2\text{S}$  and tetralin at  $380^\circ\text{C}$ , with the formation of pyrrhotite having a particle size of several hundred nanometers.<sup>17</sup> However, in the presence of coal, sulfiding produces a much smaller particle size pyrrhotite<sup>6</sup> which has also been observed on Fe-impregnated carbon black.<sup>18</sup>

Approximately 95% of the Fe contained in the residue isolated from runs to which 1.2 wt % Fe was added as SFIO was present as the oxide, even though the amount of sulfur present in the coal (0.39%) was sufficient to convert ~70% of the added Fe to pyrrhotite. However, pyrrhotite would only form when sulfur was added to the reaction mixture. In runs to which a 3-fold excess of sulfur was added along with 1.2 wt % Fe, >95% of the Fe was converted to pyrrhotite within 7.5 min, indicating that when sulfur was present pyrrhotite formed rapidly and was present during almost all of the reaction period. Since particle size of the resulting pyrrhotite was previously reported to be related to the size of the original oxide, SFIO should provide pyrrhotite having a smaller size with correspondingly higher surface area than IO.

As seen in Table II, THF conversion increased when Fe oxides were added to the reaction mixture, while adding sulfur along with the Fe oxides further increased conversion. In the absence of sulfur at 30 minutes runtime, adding SFIO and IO resulted in conversions of 83.4 and 80.2%, respectively, relative to a conversion of 76.7% in the absence of added Fe oxides. The increase was greater for SFIO suggesting a response to the higher surface area. Reactions in which sulfur was added follow the same pattern with SFIO giving higher conversion. At 30 min, addition of sulfur to SFIO and IO increased conversions to 85.4 and 83.6%, respectively, while at 60 min, conversions were 88.8 and 87.0%, respectively.

Oils yields responded quite differently to addition of Fe oxide in the absence of added sulfur. In both cases shown, they actually decreased somewhat, resulting in a buildup of PA+A. When SFIO and IO were present in the 30 min runs, Oils yields decreased to 29.7 and 26.2%, respectively, relative to a yield of 31.8% in the absence of added Fe. When sulfur was added, oil yields increased for both Fe oxides. After 30 min, yields upon addition of SFIO and IO were 36.7 and 37.0%, respectively, while after 60 min, yields were 46.2 and 46.8%, respectively, compared to 42.6% in the absence of added Fe. The sulfided catalyst is clearly better than the oxide for promoting Oils yield.

Adding sulfur to the reaction at the same level as in the other experiments but in the absence of any added Fe oxide caused an increase in conversion from 76.7 to 79.1% and a decrease in Oils yield from 31.8 to 28.2%. At this level of sulfur addition, the calculated initial  $\text{H}_2\text{S}$  partial pressure in the reactor at reaction temperature was 25 psig. The effect on conversion and Oils yield was similar, though less effective than adding Fe oxides in the absence of added sulfur. Since the combined addition of sulfur and Fe oxides was superior to the addition of the Fe oxides alone, the direct contribution from adding sulfur at this level (equivalent to ~1%  $\text{H}_2\text{S}$  in  $\text{H}_2$ ) is small relative to its effect on the chemistry of the Fe in the reaction.

Total H consumption in these reactions was determined from analysis of dihydrogen ( $\text{H}_2$ ) in the gaseous product and the H remaining in the solvent. The latter was calculated from a determination of the change in ratio of naphthalene to tetralin in the pentane soluble fraction. Total H consumption appeared not to increase upon addition of SFIO or IO in the absence of sulfur. Adding sulfur with the Fe oxide had little effect on hydrogen consumption using IO, but a significant effect on hydrogen consumption with SFIO. Total H consumption, based upon maf coal, in the presence of SFIO in the 30 min runs increased from 36 mg/g in the

absence of sulfur to 45 mg/g when sulfur was added. The consumption of  $H_2$  from the gas phase reflected this increased activity. In the 30 min runs, reaction of coal in the absence of additives and in the presence of SFIO gave  $H_2$  consumptions of 23 and 24 mg/g, respectively. Adding sulfur to the SFIO increased  $H_2$  consumption to 37 mg/g. Similar activity changes were observed for the 60 min runs.

The effect of adding 14% of a high surface area carbon (90  $m^2/g$ ) on conversion, product yields and H consumption was negligible. Even though the available  $N_2$  BET surface area was more than double the surface area from adding SFIO at a 1.2% Fe level, the reaction did not change. Clearly, the catalytic effect of adding SFIO is not merely a response to added surface area.

### Conclusions

Conversion of Wyodak coal to THF soluble product increases in the presence of added Fe oxide, regardless of the presence of sulfur. The higher surface area SFIO is more active than IO for conversion. Both SFIO and IO increase Oils yields when sulfur is added but have little effect in its absence. Since addition of sulfur to coal in the absence of added Fe oxides had little effect on the reaction, the mechanism by which sulfur affects the reaction is presumed to be through sulfiding the Fe. Total H consumption was affected only when both SFIO and sulfur were added to the reaction. The other cases showed little response. The contribution of tetralin to the amount of H consumed in the reaction appears to be relatively constant for reaction times of 30 and 60 min suggesting the reaction pathway involving H-transfer from solvent to coal is important early in the reaction sequence. The effect of SFIO with sulfur, the catalyst that significantly improved H consumption, is to increase direct  $H_2$  addition to the product. The absence of any effect of adding high-surface area carbon indicates that surface area alone is not responsible for the improvement from adding the Fe-oxides.

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Table I. Black Thunder Coal Analysis			
Proximate Analysis		Ultimate Analysis	
	(wt%, as-determined)		(wt%, dry)
Moisture	21.2	Carbon	68.68
Ash	5.15	Hydrogen	4.76
Volatile Matter	34.4	Nitrogen	1.21
Fixed Carbon	39.3	Sulfur	0.56
Sulfur Types		Oxygen (diff)	18.25
Total	0.39	Ash	6.54
Pyritic	0.07	Ash, SO <sub>3</sub> -free	5.42
Sulfate	0.09		
Organic	0.23		

Table II. Product distribution from liquefaction of Wyodak coal in tetralin <sup>a</sup>									
Catalyst	none			SFIO			IO		
Added Fe, wt% mf Coal	0	0	0	0	1.2	1.2	1.2	1.1	1.2
S/Added Fe mol/mol	0	0	-	-	0	3.0	0	3.0	3.0
H <sub>2</sub> S Partial Pressure at temperature, psi			25	24					
Reaction time, minutes	30	60	30	60	30	30	30	30	60
Products, wt% maf Coal									
HC Gases	0.7	1.0	1.1	1.3	0.8	1.4	2.0	1.4	1.7
CO+CO <sub>2</sub>	5.3	5.2	6.7	5.7	5.3	5.1	7.1	5.1	4.9
Oils	31.8	42.6	28.2	34.0	29.7	36.7	46.2	26.2	46.8
PA+A	38.9	35.4	43.1	42.2	47.6	42.2	33.5	47.1	33.6
IOM	23.3	15.8	20.9	16.8	16.6	14.6	11.2	19.8	13.0
THF Conversion	76.7	84.2	79.1	83.2	83.4	85.4	88.8	80.2	87.0
n:t ratio	0.26	0.26	0.32	0.40	0.19	0.14	0.16	0.29	0.24
Hydrogen consumed, mg/g maf Coal									
from gas	23	30	19	21	24	37	52	22	35
from solvent	15	15	18	21	12	8	10	16	14
Total	38	45	37	42	36	45	62	38	49
<sup>a</sup> Liquefaction experiments at 415°C using 3 g Black Thunder coal, 5.4 g tetralin, 6.89 MPa H <sub>2</sub> cold. SO <sub>2</sub> free ash basis. <sup>b</sup> 14% carbon black added (mf coal basis, no Fe).									